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Aqueous-Phase Oxidation: Rate Enhancement Studies

Richard S. Willms,[†] Danny D. Reible, David M. Wetzel, and Douglas P. Harrison*

Department of Chemical Engineering, Louisiana State University, Baton Rouge, Louisiana 70803

In an effort to discover techniques for increasing intrinsic aqueous-phase oxidation rates, the rate of *m*-xylene oxidation has been studied at 400–473 K and 13.8 MPa in the presence of hydrogen peroxide and phenol. At these conditions, hydrogen peroxide decomposes instantaneously to produce free radicals necessary to initiate the *m*-xylene oxidation, thereby greatly reducing or even eliminating the induction period normally associated with *m*-xylene oxidation. Once the peroxide radicals are consumed, however, the *m*-xylene oxidation rate in the rapid reaction phase returns to the values expected in the absence of peroxide. Addition of more easily oxidized phenol to *m*-xylene produces a synergizing effect in which cross-initiation greatly enhances the *m*-xylene oxidation rate. The length of the *m*-xylene induction phase is greatly reduced, approaching the intrinsic phenol induction time, and the rapid reaction-phase rate constant for *m*-xylene can be increased by almost 2 orders of magnitude compared to the rate constant for *m*-xylene reacting alone.

Although aqueous-phase oxidation is now used for wastewater treatment in more than 200 plants worldwide (Canney et al., 1984), the process is limited by the relatively slow rates at which the oxidation reactions occur. Long residence times (≈ 3600 s) and relatively severe temperatures (400–600 K) and pressures (5–15 MPa) are required.

A number of methods have been investigated to increase the oxidation rates, with catalyzed aqueous-phase oxidation receiving the most attention. For example, Brett and Gurnham (1973) studied the effect of metal salts on the oxidation of glucose. Chowdhury and Ross (1975) found that CuSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ catalysts increased the oxidation rate of "strong wastewater" by a factor of 2–3 over the uncatalyzed oxidation rate. Sadana and Katzer (1974) claim that supported and unsupported copper oxide was capable of enhancing the aqueous-phase oxidation of phenol.

More recently, Miller and Swientoniewski (1982) studied the oxidation of 15 organics in the presence of a patented catalyst containing bromide, nitrate, and manganese ions in acidic solution. Most of the organics were destroyed effectively, but the authors did not report rate data. Reaction products such as bromoxylene and dibromoxylene were reported leading one to question the exact role of the catalyst. Baillod and Faith (1983) found that a copper catalyst increased the rate of oxidation of phenol, 2-chlorophenol, and 4-nitrophenol by a factor of 2–3.

While it is reasonably clear that a catalyzed aqueous-phase oxidation is possible, the level of rate enhancement so far reported is disappointing. Further, the use of a catalyst, either homogeneous or heterogeneous, to treat a waste stream raises further problems. Homogeneous catalysts must be recovered before the stream can be discharged, both for environmental and economic reasons. Heterogeneous catalysts are likely to suffer rapid deactivation in the "dirty" waste stream environment.

In this paper we report preliminary results using two alternate methods of rate enhancement, initiation and synergism.

Initiation. Aqueous-phase oxidation reactions generally proceed according to a free-radical mechanism and are

characterized by an induction period followed by a rapid reaction phase. During the induction period, initiation reactions gradually increase the free-radical concentration until propagation becomes the dominant process. The addition of free-radical initiators, such as peroxides and azo compounds (Emanuel et al., 1967), is known to be effective in reducing the length of the induction period. Only small amounts of the initiator are required, as the majority of the organic reaction is not with the initiator but through chain propagation spawned by the initiator.

There are a number of papers on the use of initiators in liquid-phase oxidation in an organic solvent. Furthermore, the addition of hydrogen peroxide has also been reported in aqueous-phase oxidation studies (Chowdhury and Ross, 1975; Brett and Gurnham, 1973). In both of these cases, however, a catalyst and peroxide were added simultaneously so that the individual effects are difficult to distinguish. Only one paper has been located which deals strictly with the initiation of aqueous-phase oxidation. Shibaeva et al. (1969b) studied the aqueous-phase oxidation of phenol using hydrogen peroxide at a pH of 1.5. At these acidic conditions, the dissociation of hydrogen peroxide is much slower than in a neutral solution. Intrinsic rate constants were found to be enhanced by 1–2 orders of magnitude by the presence of peroxide.

Synergism. Synergism, as used here, involves the simultaneous reaction of at least two species, one easily oxidized and the other more refractory, with the easily oxidized component effectively increasing the oxidation rate of the refractory compound. Synergism may have been present in previous studies which examined the aqueous-phase oxidation of mixtures such as pulping liquor; however, no analysis was possible because of the complexity of the feedstock. Only one investigation of aqueous-phase synergism under carefully controlled conditions is known. Shibaeva et al. (1969a) determined that the benzene oxidation rate was increased by the presence of phenol in experiments conducted at 453–513 K.

Experimental Section

In both the initiation and synergism studies, *m*-xylene served as the base component. Hydrogen peroxide was used as the free-radical initiator, while phenol, which is oxidized more readily than *m*-xylene, served as the syn-

[†] Present address: Los Alamos National Laboratory, Los Alamos, NM 87545.

ergizing agent. The aqueous-phase oxidation kinetics of both *m*-xylene and phenol reacting alone have been reported previously (Willms et al., 1987), and these results serve as the basis for comparison of the rate enhancement effects.

Both the experimental apparatus and basic operating procedures have been described previously (Willms et al., 1985). For these rate enhancement studies, no equipment modifications were necessary, and only minimal changes in the procedure were adopted. The reactor was first charged with 700 mL of distilled water and then heated and pressurized as previously reported. *m*-Xylene and either hydrogen peroxide or phenol were flushed into the reactor using 80 mL of distilled water. In past work the flush water was preheated to just below reaction temperature to minimize temperature upsets at the beginning of the experiment. However, when hydrogen peroxide was added, the water was not preheated so that premature decomposition of the peroxide would not occur.

Approximately 10^{-4} kg of *m*-xylene was added in each run with varying amounts of hydrogen peroxide or phenol. The reacting solution was analyzed periodically by direct injection of 1- μ L samples into a gas chromatograph using a Valco high-pressure sampling valve. Five milliliters of reacting liquid was flushed through the valve just prior to each sample to ensure that the sample was representative of the reactor contents at that time. Only the concentrations of the parent organics (*m*-xylene and phenol) were monitored. No effort was made to separate oxidation intermediates and products as the additional analytical complexity would have severely limited the frequency at which samples could be obtained during a run. No hydrogen peroxide analysis was attempted because dissociation was instantaneous at reaction conditions. Details of the chromatographic conditions have been published (Willms et al., 1987).

The data were analyzed by using the reaction-phase equilibrium model previously published (Willms et al., 1985). This model allows determination of intrinsic kinetic parameters from experimental data complicated by vapor-liquid equilibrium and mass-transfer effects. Key assumptions of the model include Henry's law partitioning of volatile organics between phases and sufficiently rapid mass transfer so that a dynamic phase equilibrium is maintained at all times. The initiation reaction was taken to be zero-order in organic and first-order in dissolved oxygen, while the kinetics during the rapid reaction phase was assumed to be first-order in organic and half-order in dissolved oxygen. These reaction orders were previously determined for the pure components (Willms et al., 1987). While the experimental program of this study was not sufficient for complete verification of the reaction orders, none of the data was inconsistent with these kinetics. The resultant model contains two parameters, the time corresponding to the end of the induction phase, t_s , and the intrinsic rate constant, k_r . The correlating equations for the two parameters are (Willms et al., 1987)

induction phase

$$t_s(\text{O}_2) = [(R^*)_s/A_i] \exp[E_i/RT] \quad (1)$$

rapid reaction phase

$$d(\text{RH})/dt = -k_r(\text{O}_2)^{1/2}(\text{RH}) \quad (2)$$

with

$$k_r = A_r \exp[-E_r/RT] \quad (3)$$

In this paper the superscript *i* will be added to these pa-

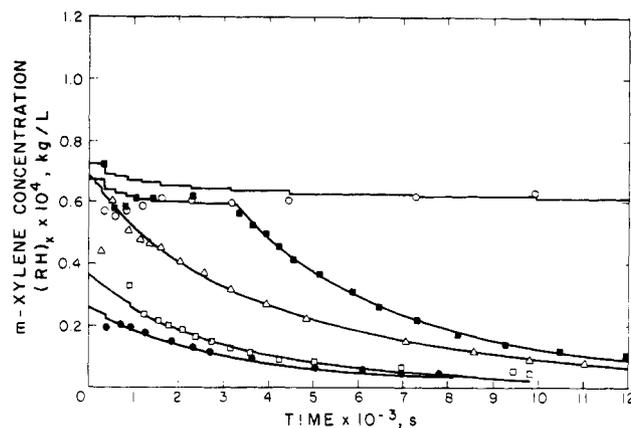
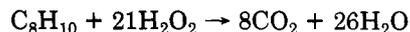


Figure 1. Time-concentration results for *m*-xylene at 473 K and 13.8 MPa as a function of H_2O_2 concentration (% stoichiometric): (○) 0.025%; (■) 0.25%; (△) 0.5%; (□) 2.5%; (●) 25.0%.

rameters to designate values determined in the presence of H_2O_2 initiator, while the superscript *s* will be used to designate values obtained from the *m*-xylene/phenol synergism studies.

Initiation Results

A series of experiments was performed to examine the separate effects of hydrogen peroxide concentration and temperature on *m*-xylene oxidation, all at constant reactor pressure. The hydrogen peroxide concentration is reported as percent of stoichiometric, based upon the amount of hydrogen peroxide required for the direct and complete oxidation of *m*-xylene added according to the reaction



Thus, 21 mol of hydrogen peroxide is required to completely oxidize 1 mol of *m*-xylene (or 6.74 g of $\text{H}_2\text{O}_2/\text{g}$ of C_8H_{10}). The range of H_2O_2 concentrations studied was 0.025–25% stoichiometric, with the majority of runs being at the lower end of the concentration range.

The result of adding various quantities of H_2O_2 on *m*-xylene destruction at 473 K and 13.8 MPa is illustrated in Figure 1. At the lowest H_2O_2 concentration (0.025% stoichiometric), there is no apparent effect; the initial *m*-xylene concentration is consistent with the quantity of *m*-xylene added, and the extremely long induction period is consistent with results obtained in the absence of the initiator (Willms et al., 1987). Increasing the amount of H_2O_2 to 0.25% stoichiometric clearly shortens the induction time, and a further increase to 0.5% effectively removes the induction period altogether. Still higher levels of H_2O_2 not only result in zero induction time but also decrease the initial *m*-xylene concentration. Thus, 0.5% stoichiometric addition of H_2O_2 appears to provide the critical minimum number of free radicals necessary to erase the induction period at this temperature (473 K), while excess free radicals formed by larger H_2O_2 additions react instantaneously with the *m*-xylene, thereby reducing the initial concentration. The good agreement between the model and experiment during the rapid reaction phase tends to confirm the assumption that the rapid reaction-phase kinetics are first-order in organic.

The effect of temperature from 436 to 473 K was studied at constant H_2O_2 concentration. *m*-Xylene concentrations as a function of time at three of the temperatures studied are shown in Figure 2. The H_2O_2 concentration of 2.5% stoichiometric was sufficiently high to eliminate the induction period at all temperatures. The selection of this initial H_2O_2 concentration was based upon an exploratory run at 448 K which utilized 0.5% stoichiometric H_2O_2 , the

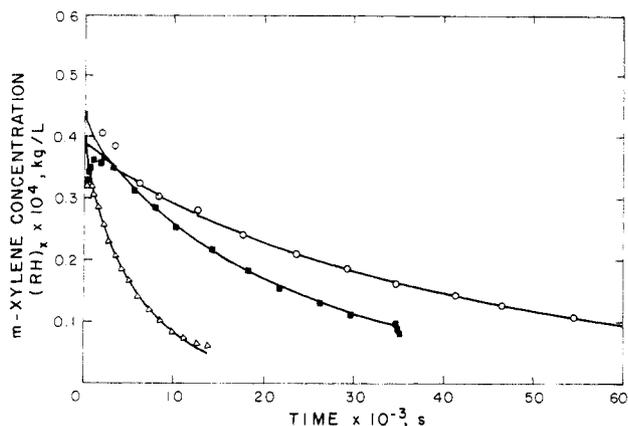


Figure 2. Time-concentration results for *m*-xylene at 13.8 MPa and 2.5% stoichiometric H_2O_2 as a function of temperature: (O) 436, (■) 450, (Δ) 466 K.

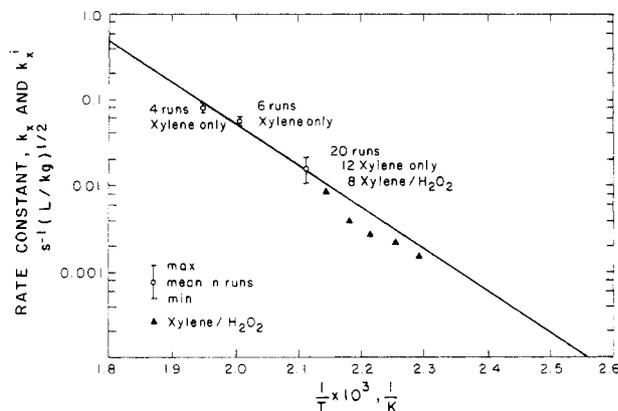


Figure 3. Arrhenius analysis for *m*-xylene initiated with H_2O_2 : rapid reaction-phase rate constant, $k = A \exp[-E/RT]$. *m*-Xylene only: $A = 1.19 \times 10^8 \text{ [L/(s}^2 \text{ kg)]}^{1/2}$, $E = 89.5 \pm 8.6 \text{ kJ/gmol}$. *m*-Xylene/ H_2O_2 : $A = 3.24 \times 10^8 \text{ [L/(s}^2 \text{ kg)]}^{1/2}$, $E = 93.8 \pm 7.8 \text{ kJ/gmol}$.

critical value previously determined at 473 K. A lengthy induction period resulted ($t_s^i \geq 9 \times 10^3 \text{ s}$), thereby indicating that the critical peroxide concentration was a function of temperature. The use of 2.5% peroxide reduced the initial concentration of *m*-xylene, in the same manner as shown previously in Figure 1. Results of the model analysis are shown by the solid lines in Figure 2; once again, the agreement is quite good.

A comparison of the values of k^i at 473 K with those previously reported for *m*-xylene reacting alone (Willms et al., 1987) indicates no significant difference between the two groups. The average k^i for eight H_2O_2 -initiated runs at 473 K was $0.0148 \text{ s}^{-1} \text{ (L/kg)}^{1/2}$ (range 0.0106–0.0184) compared to the Arrhenius values of k of $0.0154 \text{ s}^{-1} \text{ (L/kg)}^{1/2}$ reported for *m*-xylene reacting alone. Further evidence that the H_2O_2 has no long-term effect is provided in Figure 3, an Arrhenius plot of the rapid reaction-phase rate constant for all *m*-xylene oxidations, initiated and uninitiated. The least-squares line through the combined data represents an activation energy of $93.8 \pm 7.8 \text{ kJ/gmol}$ (confidence limits are at the 95% level), not significantly different from the value of $89.5 \pm 8.6 \text{ kJ/gmol}$ previously reported (Willms et al., 1987) for *m*-xylene reacting alone.

Perhaps the most striking result of this initiation study is the fact that oxidation occurs at all at the lower temperatures. Without an initiator, the induction time at 436 K and 13.8 MPa is estimated to be $2.8 \times 10^5 \text{ s}$ (by extrapolation of the uninitiated *m*-xylene results), compared to the zero experimental induction time in the presence of 2.5% stoichiometric peroxide initiator. Once initiated

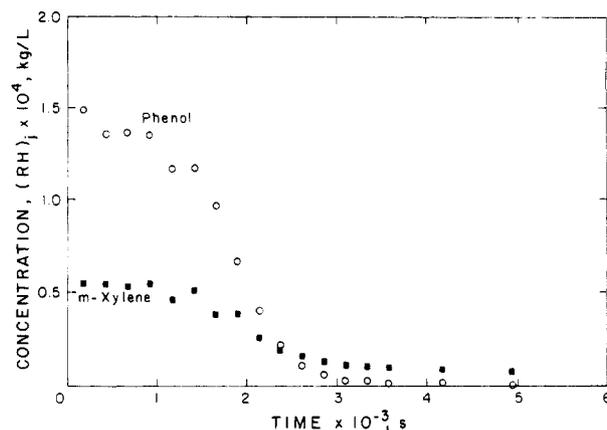


Figure 4. Typical time-concentration results for *m*-xylene and phenol reacted simultaneously.

with a small amount of hydrogen peroxide, the propagation reactions are self-sustaining at these lower temperatures, with a rate consistent with that expected from extrapolation of the higher temperature results in the absence of an initiator.

The concept of the critical concentration of initiator needed to start the propagation reactions at each temperature is consistent with an interpretation presented by Emanuel et al. (1967). They argue that a steady-state, equilibrium concentration of free radicals, independent of the initial concentration, is eventually achieved. When the initial concentration of radicals is zero, the concentration increases with time (induction period) to the equilibrium value. When the initial concentration exceeds the equilibrium value, the radical concentration decays with time to the equilibrium value. In this case the decay appears to be essentially instantaneous as the excess radicals react directly with a portion of the *m*-xylene.

Synergism Results

In a previous paper, Willms et al. (1987) showed that, when reacted separately, phenol was much more reactive than *m*-xylene at equivalent conditions of temperature and pressure. For example, at 473 K and 13.8 MPa, the induction period for *m*-xylene was approximately 10^4 s compared to 250 s for phenol. Further, during the rapid reaction phase, the phenol rate constant at these conditions was approximately 100 times the *m*-xylene rate constant.

When phenol and *m*-xylene are reacted simultaneously, the results are quite different as shown in Figure 4 for a run at 443 K and 13.8 MPa. Both reactions are characterized by the familiar induction phase followed by the rapid reaction period. However, the duration of the *m*-xylene induction phase in this example is about 1400 s, approximately equal to the length of the phenol induction phase and only about 2% of the expected induction period for *m*-xylene reacting alone. Similarly the *m*-xylene rate constant in the rapid reaction phase is increased by a factor of approximately 20. The results shown in Figure 4 are typical of those found in all tests where *m*-xylene and phenol were reacted simultaneously.

The results may be interpreted qualitatively on the basis of cross-initiation. When *m*-xylene and phenol react simultaneously, both generate free radicals, with the majority originating from phenol. Assuming that the parent compounds are capable of reacting with radicals generated from either parent, cross-initiation will occur and the oxidation rate of *m*-xylene will be increased since the total radical concentration is greater than when *m*-xylene is reacted alone; the oxidation rate of phenol will decrease

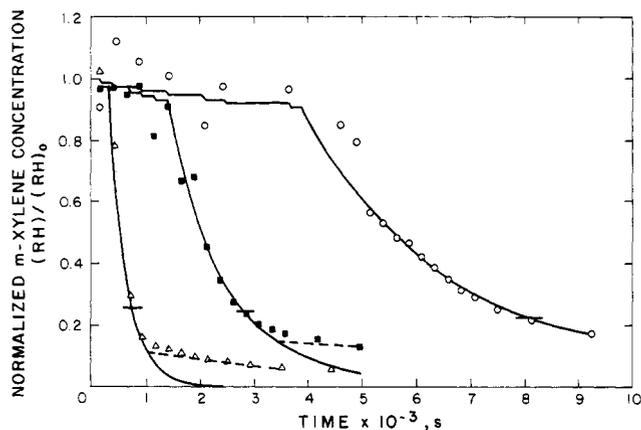


Figure 5. Time-concentration results for *m*-xylene at 13.8 MPa with equimolar phenol as a function of temperature: (O) 427, (■) 443, (Δ) 466 K.

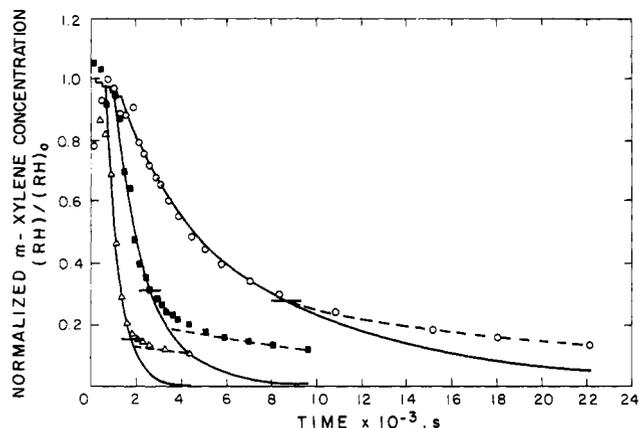


Figure 6. Time-concentration results for *m*-xylene at 451 K and 13.8 MPa as a function of phenol concentration (% equimolar): (O) 15%; (■) 50%; (Δ) 100%.

since *m*-xylene has consumed some of the phenol radicals.

All runs in which *m*-xylene and phenol were reacted simultaneously were conducted at 13.8 MPa, with temperature and initial phenol concentration serving as the variables. The overall temperature range was 387–473 K while three levels of initial phenol concentration were investigated: (a) 0.89 kg of phenol/kg of *m*-xylene (equimolar); (b) 0.44 kg of phenol/kg of *m*-xylene (50% equimolar); and (c) 0.13 kg of phenol/kg of *m*-xylene (15% equimolar). It is important to note that only at the highest temperature (473 K) is *m*-xylene capable of being oxidized in reasonable times when present alone in the reacting mixture, whereas in the presence of phenol the oxidation rate of *m*-xylene will be shown to be appreciable at temperatures as low as 400 K.

***m*-Xylene Kinetics.** Figures 5 and 6 give representative concentration–time results for *m*-xylene, with Figure 5 showing the effect of temperature at constant initial phenol concentration and Figure 6 showing the effect of initial phenol concentration at constant temperature. Consistent with previous results, increasing the temperature both shortens the induction period and increases the reaction rate during the rapid reaction phase. Addition of phenol shortens the induction period in a manner similar to that observed when H₂O₂ initiator is added; however, unlike the peroxide, the effect of phenol persists into the rapid reaction phase where the *m*-xylene oxidation rate is considerably enhanced.

Values of the length of the induction period, t_{sx}^s , and the intrinsic rate constant, k_x^s , during the rapid reaction

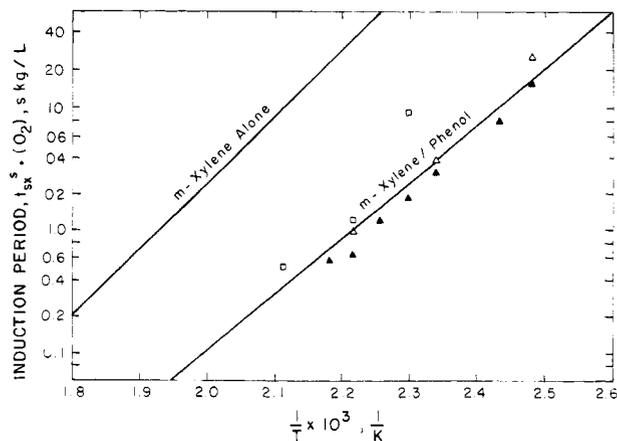


Figure 7. Arrhenius plot for the synergized *m*-xylene induction phase as a function of phenol concentration (% equimolar): (□) 15%; (Δ) 50%; (▲) 100%.

phase for *m*-xylene were determined by using the reaction model previously discussed. Reliable values could not be determined at the highest temperature and phenol concentration because the reaction was so fast that insufficient data could be collected to permit a meaningful regression. At the lowest temperature, the duration of the induction phase was so great that the run was terminated before the rapid reaction phase was reached. As with pure component oxidation, it was assumed that rapid phase reaction rates were one-half-order with respect to oxygen to allow the calculation of the intrinsic rate constant, k_x^s , from the pseudo-first-order rate constant, k'_x^s .

Near the end of the reaction, both Figures 5 and 6 show that the *m*-xylene concentration does not decrease as rapidly as the model predicts. This “tailing” appears to coincide with the effective disappearance of phenol. The times at which the phenol concentration drops to 5% of its initial value are noted in Figures 5 and 6 by the horizontal slashes. The onset of significant deviation between the model and experiment roughly corresponds to those times. The reduction or cessation of phenol cross-initiating *m*-xylene propagation chains is thought to be the cause of the decrease in reaction rate. Certainly, in the limit of zero phenol concentration, the *m*-xylene rate should return to its slower, unsynergized value. For comparison purposes, the dashed lines in Figures 5 and 6 represent the model predictions using the pure component (unsynergized) values of the intrinsic *m*-xylene rate constant beginning at the indicated time and concentration. Thus, it appears that a transition period exists, beginning approximately at the time that the phenol concentration is reduced to 5% of its initial value and ending when the rate of *m*-xylene oxidation returns to its unsynergized level.

Arrhenius plots for the duration of the induction period, t_{sx}^s , and the synergized rate constant, k_x^s , for *m*-xylene reacting in the presence of phenol are shown in Figures 7 and 8, respectively. For reference purposes, both figures also contain the pure component results previously reported (Willms et al., 1987), with the Figure 8 pure component line also including the peroxide-initiated results from the previous section (Figure 3). From Figure 7 it is clear that phenol addition reduces the *m*-xylene induction period by greater than 1 order of magnitude and that the synergized induction time is, at most, only marginally dependent on initial phenol concentration. All experimental results at the highest phenol concentration show slightly lower induction times, but the difference is small. The Arrhenius line is drawn through the entire data set, and the resultant activation energy is 88.4 ± 19.2 kJ/gmol.

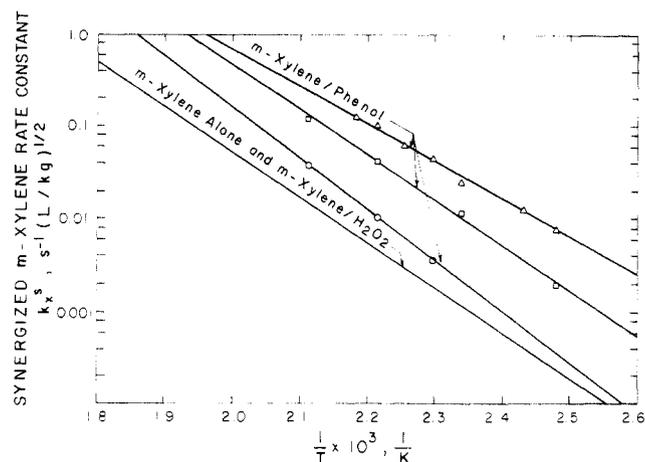


Figure 8. Arrhenius plot for the synergized *m*-xylene rapid reaction rate constant as a function of phenol concentration (% equimolar): (O) 15%; (□) 50%; (Δ) 100%.

Table I. Summary of Kinetic Parameters for *m*-Xylene-Phenol Synergism

induction period: $t_{s_j}^a(O_2) = [(R^*)_s/A_{ij}] \exp[E_{ij}/RT]$				
	$(R^*)_s/A_{ij}$, kg s/L		E_{ij} , kJ/gmol ^a	
<i>m</i> -xylene				
alone	4.5×10^{-11}		103 ± 20	
with phenol	6.2×10^{-11}		88 ± 19	
phenol				
alone	9.4×10^{-12}		94 ± 31	
with <i>m</i> -xylene	2.9×10^{-11}		90 ± 12	
rapid reaction period: $d(RH)_j/dt = -A_{rj}(O_2)^{1/2}(RH)_j \exp[-E_{rj}/RT]$				
	A_{rj} , [L/(s ² kg)] ^{1/2}		E_{rj} , kJ/gmol ^a	
	<i>m</i> -xylene	phenol	<i>m</i> -xylene	phenol
<i>m</i> -xylene				
alone and with H ₂ O ₂	3.2×10^8		94 ± 8	
with 15% equimolar phenol	2.1×10^{10}	1.8×10^{11}	106 ± 7	114 ± 93
with 50% equimolar phenol	3.3×10^9	2.7×10^9	94 ± 26	92 ± 6
with 100% equimolar phenol	1.0×10^8	8.5×10^8	78 ± 22	85 ± 7
phenol				
alone	3.7×10^{12}		112 ± 13	

^a All confidence limits are at the 95% level.

Much of the uncertainty is associated with the single data point furthest removed from the Arrhenius line. If this point is removed from the analysis, the 95% confidence limits are reduced to ± 12.7 kJ/gmol without significantly changing the mean value. Further, in the following section, it will be shown that the length of phenol induction period is largely unaffected by the presence of *m*-xylene and that the length of the induction period for *m*-xylene is only slightly greater than the intrinsic phenol induction time.

Figure 8 shows that the addition of phenol increases the rate of *m*-xylene oxidation during the rapid reaction phase, with the magnitude of the rate enhancement dependent upon phenol concentration. The addition of equimolar phenol concentrations produces a greater than 1 order of magnitude increase in the *m*-xylene rate constant, with smaller additions of phenol producing proportionally smaller increases. The activation energies for each phenol concentration are quite similar (see Table I) and certainly within the statistical confidence limits of each group.

Phenol Kinetics. The effect of temperature on the time-concentration behavior of phenol in the presence of equimolar initial concentrations of *m*-xylene is shown in

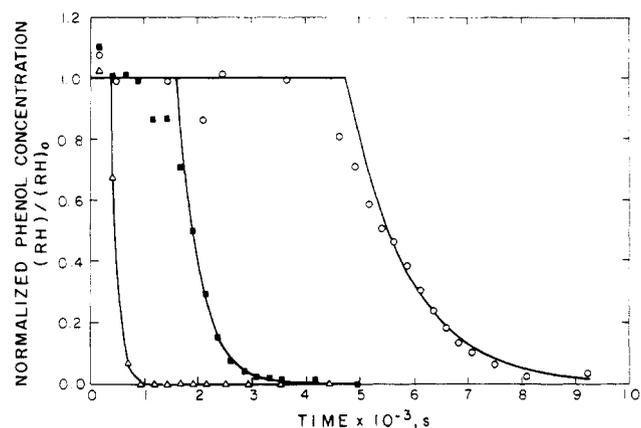


Figure 9. Time-concentration results for phenol at 13.8 MPa and equimolar *m*-xylene as a function of temperature: (O) 427, (■) 443, (Δ) 466 K.

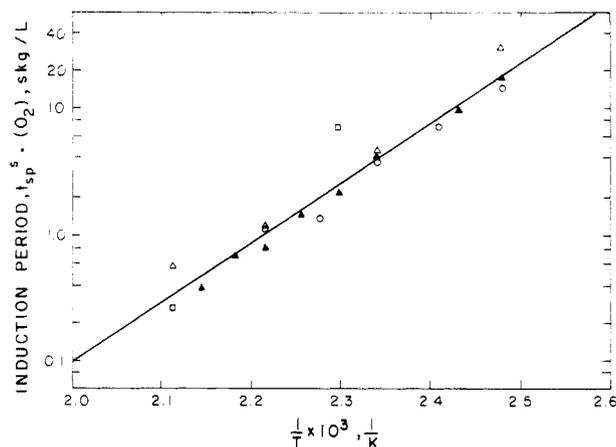


Figure 10. Arrhenius plot for the synergized phenol induction phase at 13.8 MPa as a function of phenol concentration (% equimolar): (O) phenol alone; (□) 15%; (Δ) 50%; (▲) 100%.

Figure 9. These data are from the same runs as the *m*-xylene results shown previously in Figure 5. The constant concentration during the induction period is the result of the assumption that Henry's constant for phenol at these conditions is zero, implying that the amount of phenol in the vapor phase is negligible. It is obvious from Figure 9 that the model provides a good fit with the experimental data, even to very low phenol concentrations.

An Arrhenius plot of the length of the phenol induction period in the presence of *m*-xylene is shown in Figure 10. This figure also contains results of the pure component phenol studies previously reported (Willms et al., 1987). The activation energy for phenol alone was reported previously to be 94 ± 31 kJ/gmol. The activation energy for the combined data is 90 ± 12 kJ/gmol (Table I). Thus, at least over the concentration and temperature ranges studied here, the presence of *m*-xylene has no effect on the phenol induction time. By comparing the Arrhenius lines for synergized *m*-xylene from Figure 7 and for phenol from Figure 10, we find that the ratio of the length of the *m*-xylene and phenol induction times is approximately 1.25.

Figure 11 is an Arrhenius plot of the synergized phenol rate constant during the rapid reaction phase; the effect of *m*-xylene in inhibiting the rate of phenol oxidation is clearly visible. However, the negative effect of *m*-xylene on phenol is less than the positive effect of phenol on *m*-xylene. With equimolar initial concentrations at 473 K, the *m*-xylene rate constant is increased by a factor of 16, while the phenol rate constant is decreased by a factor of less than 5. All kinetic parameters for both the in-

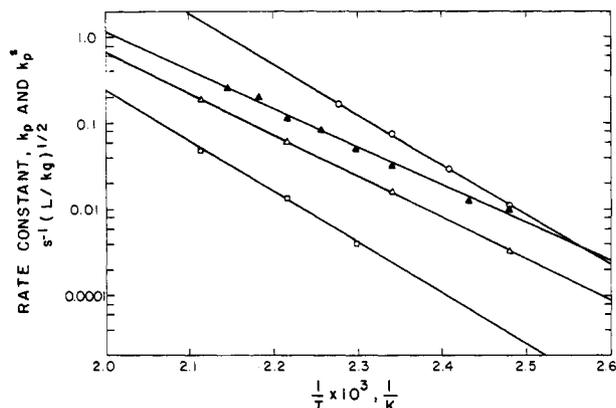


Figure 11. Arrhenius plot for the synergized phenol rapid reaction-phase rate constant as a function of phenol concentration (% equimolar): (O) phenol alone; (□) 15%; (Δ) 50%; (▲) 100%.

duction and rapid reaction periods for *m*-xylene and phenol, reacting separately (Willms et al., 1987) and together, are summarized in Table I.

Enhancement Factor

In order to quantify the effect of phenol/*m*-xylene synergism, an enhancement factor for component *j* reacting in the presence of a second component is defined by

$$En_j = k_j^s/k_j \quad (4)$$

By use of this definition, the time during the rapid reaction phase required to reduce the concentration of component *j* from the initial value, $(RH_j)_0$, to a desired final value, $(RH_j)_t$, is given by

$$t_j^s = \int_{(RH_j)_0}^{(RH_j)_t} [-En_j k_j (O_2)^{1/2} (RH_j)]^{-1} d(RH_j) \quad (5)$$

In the binary system of *m*-xylene and phenol, we have seen that the interaction is such that $En_x \geq 1$ and $En_p \leq 1$. Thus, simultaneous reaction decreases t_x^s and increases t_p^s . The minimum overall reactor residence time will occur when

$$t_x^s = t_p^s \quad (6)$$

In principle, if the initial concentration of *m*-xylene, $(RH_x)_0$, and allowable discharge concentrations of both *m*-xylene, $(RH_x)_t$, and phenol, $(RH_p)_t$, are known, the optimum initial concentration of phenol, $(RH_p)_0$, which will produce the minimum reaction time can be calculated. For initial phenol concentrations higher than this value, the overall reaction time would be determined by the time required to reduce the phenol concentration to the allowable final value. For lower initial phenol concentrations, the overall reaction time would be determined by the *m*-xylene kinetics.

The limitation of this analysis is, of course, the fact that En_j is not known over the range of concentrations of interest. As a first step in evaluating En_j for a binary mixture, consider the limits of En_j at the two concentration extremes, pure *m*-xylene and pure phenol. It is obvious that

$$\lim_{X_j \rightarrow 1} En_j = 1 \quad (7)$$

where $X_j = (RH_j)/[(RH_j) + (RH_k)]$. Further, as the concentration of *j* approaches zero, component *k* should react as if no *j* is present, and it is logical to assume that cross-initiation will cause the few molecules of *j* to be

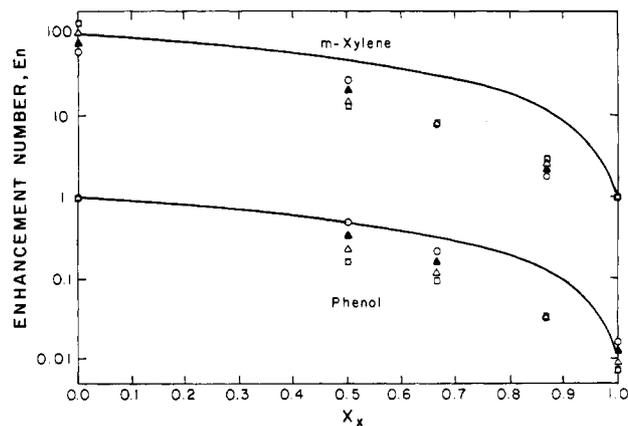


Figure 12. Enhancement number for *m*-xylene-phenol synergized reactions. Temperature: (□) 498, (Δ) 473, (▲) 443, (O) 423 K.

“swept along” at a rate equal to that of component *k*. Thus,

$$\lim_{X_j \rightarrow 0} En_j = k_k/k_j \quad (8)$$

Enhancement factors between these two limits at the specific concentrations studied were estimated from the experimental data and plotted in Figure 12.

While the range of experimental data is limited to relatively high *m*-xylene fractional concentrations ($X_x \geq 0.53$), the calculated limit points are consistent with extrapolation through the experimental data. Further, the scatter in the experimental points appears to be random, with no apparent temperature correlation.

If we define an ideal system as one in which the enhancement factor can be expressed as a linear function of fractional concentration, only pure component kinetic parameters are required to predict the mixture behavior and, consequently, solve eq 5. These linear functions between the pure component limits are shown as the curved lines on the logarithmic scale of Figure 12. Obviously, the experimental data for *m*-xylene/phenol lie below the linear function, implying nonideality and the need for mixture as well as pure component measurements.

Summary and Conclusions

Experiments have shown that the rate of destruction of *m*-xylene during aqueous-phase oxidation can be significantly enhanced by the addition of the free-radical initiator, hydrogen peroxide, or by synergism obtained through the simultaneous reaction of phenol and *m*-xylene.

At reaction conditions, hydrogen peroxide decomposes instantaneously to produce free radicals which initiate the *m*-xylene oxidation. Small concentrations of peroxide are effective in reducing the length of the induction period normally associated with *m*-xylene oxidation. Sufficiently high peroxide concentrations eliminate the induction phase altogether, and excess peroxide radicals appear to react directly and instantaneously with *m*-xylene. Once these excess radicals have been consumed, the rate of *m*-xylene oxidation during the rapid reaction phase is equal to the rate expected in the absence of the initiator.

Simultaneous reaction of refractory *m*-xylene with more easily oxidized phenol is effective in decreasing the length of the *m*-xylene induction phase and increasing the rapid phase oxidation rate as long as an appreciable concentration of phenol remains. After that time, the *m*-xylene oxidation rate decreases to the intrinsic *m*-xylene rate. Over the range of reaction temperatures and phenol concentrations studied, when *m*-xylene and phenol react si-

multaneously the *m*-xylene induction time is approximately 25% greater than the phenol induction time, and the phenol induction time is unchanged from the value previously determined for phenol reacting alone. During the rapid reaction phase, the degree of *m*-xylene rate enhancement is dependent upon the phenol concentration. For equimolar initial concentrations, the rate of *m*-xylene oxidation is enhanced by a factor of approximately 16, while the rate of phenol oxidation is retarded by a factor of approximately 4.

Both of these results can be important to the further development of the aqueous-phase oxidation process for wastewater treatment. Hydrogen peroxide addition could be used during process startup or following process upsets as a means of speeding the approach to steady-state operating conditions. The rate enhancement associated with synergism indicates possible advantages to be gained by the simultaneous treatment of multiple wastes or perhaps by purposely adding less refractory organics such as phenol. The fact that phenol is a common component of many waste streams as well as an effective rate enhancing component could have significant economic impact. Instead of having to purchase expensive reagents, a judicious combination of wastes might result in more efficient treatment of both.

Nomenclature

A = preexponential factor in the Arrhenius equation, units vary

E = activation energy, kJ/gmol

En = enhancement number defined by eq 4

k = rate constant, units vary

k' = pseudo-first-order rate constant, s⁻¹

(O₂) = dissolved oxygen concentration, mass/volume

R = gas constant

(RH) = organic concentration in solution, mass/volume

(R^{*}) = free-radical concentration in solution, mass/volume

t = time, s

T = temperature, K

X = organic concentration ratio, (RH_{*j*})/[(RH_{*j*}) + (RH_{*k*})]

Subscripts

f = final value

i = induction phase

j = component *j*

k = component *k*

p = phenol

r = rapid reaction phase

s = start of the rapid reaction phase, end of the induction phase

x = *m*-xylene

0 = initial

Superscripts

i = value obtained during initiation studies

s = value obtained during synergism studies

Registry No. H₂O₂, 7722-84-1; *m*-xylene, 108-38-3; phenol, 108-95-2.

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